Electronic Supplementary Information

Phase stability of the layered oxide, $Ca_2Mn_3O_8$; probing interlayer shearing at high pressure

Laura J. Vera Stimpson[a,b], Kevin J. W. Etherdo-Sibley[a], Christopher J. Ridley[c], Craig L. Bull[c,] and Donna C. Arnold[a,*]*

[a] School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NH, UK

[b] Faculty of Science, Engineering and Social Sciences, Canterbury Christ Church University, Canterbury, Kent, CT1 1QU, UK

[c] ISIS Neutron and Muon Source, Rutherford Appleton Laboratories, Chilton, Didcot, OX11 0QX, UK

[*] Corresponding authors Dr Donna Arnold (d.c.arnold@kent.ac.uk) and Dr Craig Bull (craig.bull@stfc.ac.uk)

Rietveld refinements were performed using the GSAS suite of programs.[1,2] Multiphase refinements were performed for 53 variables which include lattice parameters, atom positions, peak shape and background. The background was modelled with 12 terms using a shifted Chebyschev polynomial function. The peak shape was modelled using the pseudo-Voigt function (type 2 in GSAS) described by Howard, and Thompson *et al*.[3,4] The $Ca_2Mn_3O_8$ phase was fitted to the model proposed by Ansell *et al*.[5] Additional phases of Pb ($Fm\bar{3}m$) from the pressure calibrant, ZrO_2 ($P42/nmc$) and Al_2O_3 ($R\bar{3}c$) from the anvil were also refined. The U_{iso} were not refined and fixed with a value of 2.50 (U*i*/U*e**100) $Å^2$ since allowing them to refine resulted in physically unrealistic values as a result of the large number of degrees of freedom and the quality of the data. The Rietveld refinement profiles are shown in Figure S1 for data collected at 290 K and Figures S2 and S3 for data collected at 120 K. Values for the refined parameters are given in tables S1 (290 K), S2 and S3 (120 K). Figures S4 through S6 shows graphically the change in selected bond lengths and bond angles with values given in tables S4 through S6.

Table S1: *Rietveld refinement parameters for neutron diffraction data collected at 290 K between 0 GPa and 6 GPa using the PEARL diffractometer for $Ca_2Mn_3O_8$, refined using the C2/m model proposed by Ansell et al.[5] Note: U_{iso} were fixed to 0.01 $Å^2$. Values in parentheses indicate one standard deviation in the parameter.*

Parameter	**Pressure (GPa)**						
	0.092	**0.445**	**1.254**	**2.142**	**3.189**	**4.451**	**5.571**
χ^2	1.027	0.9804	0.9612	0.9329	0.666	0.8492	0.776
wRp (%)	2.42	2.39	2.42	2.24	2.76	2.43	2.42
Rp (%)	2.63	2.54	2.71	2.34	3.02	2.69	2.84
a (Å)	11.0212(6)	11.0090(6)	10.9835(6)	10.9572(6)	10.9253(7)	10.8893(6)	10.8579(7)
b (Å)	5.8468(3)	5.8423(3)	5.8315(3)	5.8197(3)	5.8054(4)	5.7900(4)	5.7764(4)
c (Å)	4.9428(3)	4.9393(3)	4.9314(3)	4.9234(3)	4.9148(4)	4.9041(4)	4.8954(4)
β (°)	109.785(4)	109.780(4)	109.773(4)	109.771(4)	109.756(5)	109.762(4)	109.750(5)
Cell Vol ($Å^3$)	299.71(3)	298.94(3)	297.23(3)	295.45(3)	293.38(4)	290.99(3)	288.97(4)
Ca (*x*,0,*z*)	0.7220(6) 0.661(1)	0.7226(6) 0.660(1)	0.7222(7) 0.663(1)	0.7226(6) 0.663(1)	0.7216(8) 0.663(2)	0.7246(7) 0.667(1)	0.7240(7) 0.664(1)
Mn1 (0,0,½)							
Mn2 (0,*y*,0)	0.251(2)	0.252(2)	0.259(2)	0.254(2)	0.250(2)	0.257(2)	0.261(2)
O1 (*x*,y,*z*)	0.0980(4) 0.2220(6) 0.3894(8)	0.0975(4) 0.2217(6) 0.3900(8)	0.0972(4) 0.2235(7) 0.3903(9)	0.0979(4) 0.2236(6) 0.3904(8)	0.0977(5) 0.2237(8) 0.391(1)	0.0983(5) 0.2227(7) 0.3942(9)	0.0986(4) 0.2241(7) 0.3910(9)
O2 (*x*,½,*z*)	0.5955(6) 0.892(1)	0.5978(6) 0.894(1)	0.5976(7) 0.894(1)	0.5965(6) 0.893(1)	0.5963(8) 0.894(1)	0.5988(7) 0.899(1)	0.5969(7) 0.907(1)
O3 (*x*,0,*z*)	0.6042(5) 0.959(1)	0.6036(5) 0.959(1)	0.6029(6) 0.961(1)	0.6032(5) 0.962(1)	0.6034(7) 0.960(1)	0.6045(6) 0.961(1)	0.6065(6) 0.965(1)

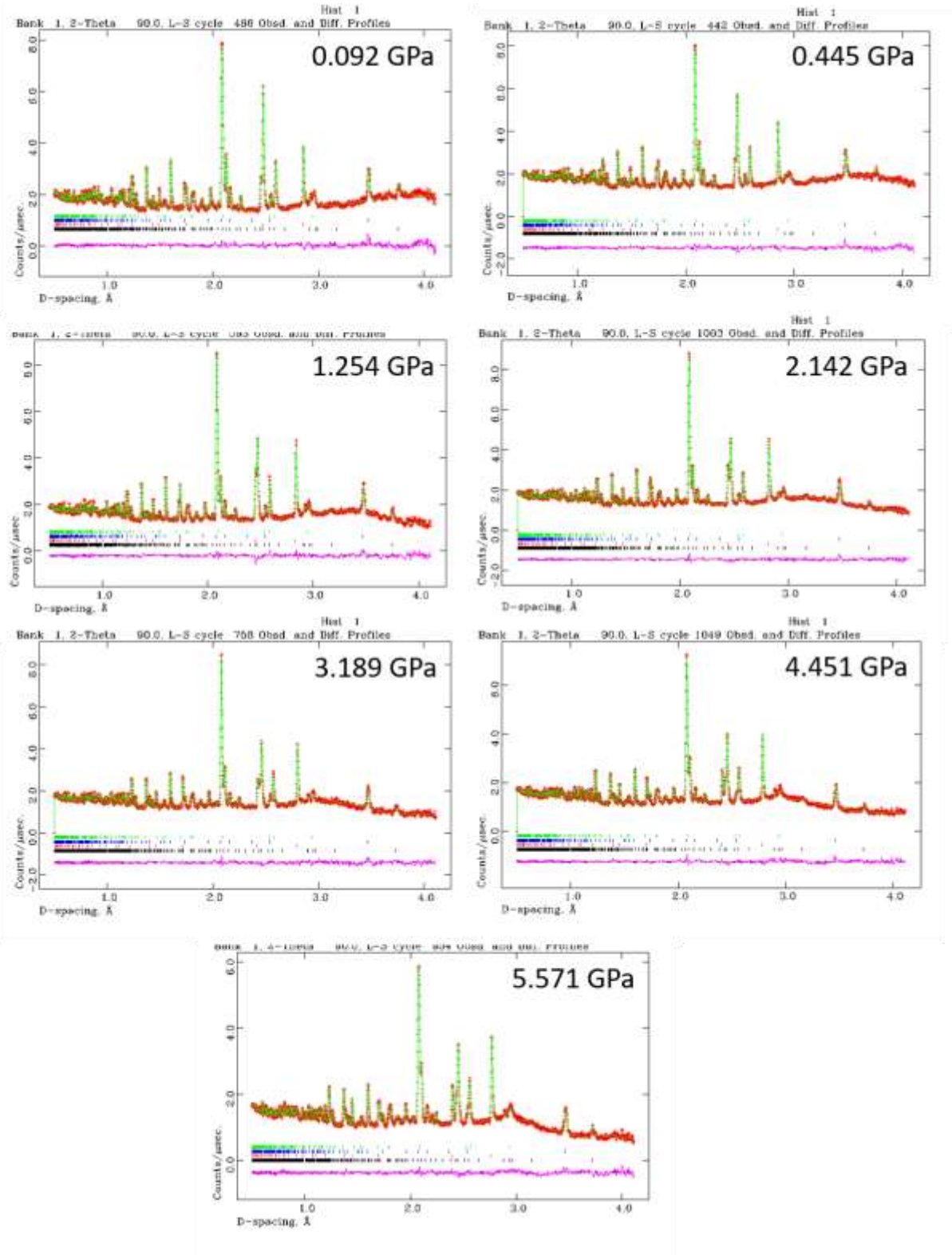

Figure S1: *Rietveld refinement of the powder neutron diffraction data collected for* $Ca_2Mn_3O_8$ *at 290 K at pressures between 0 GPa to 5.571 GPa refined using the space group C2/m and the model proposed by Ansell et al.*[5] *The red circles are the observed data, the green line is the calculated model and the pink line is the difference curve.*

Table S2: *Rietveld refinement parameters for neutron diffraction data collected at 120 K between 0 GPa and 2.193 GPa using the PEARL diffractometer for $Ca_2Mn_3O_8$, refined using the C2/m model proposed by Ansell et al.[5] Note: U_{iso} were fixed to 0.01 $Å^2$. Values in parentheses indicate one standard deviation in the parameter.*

Parameter	**Pressure (GPa)**					
	-0.002	**0.303**	**1.183**	**1.550**	**1.825**	**2.193**
χ^2	1.301	0.7835	1.114	0.736	1.198	0.8963
wRp (%)	2.42	2.66	2.26	2.95	2.41	2.93
Rp (%)	2.85	2.99	2.55	3.35	2.77	3.33
a (Å)	11.0074(5)	11.0001(6)	10.9769(6)	10.9671(9)	10.9640(8)	10.949(1)
b (Å)	5.8394(3)	5.8372(3)	5.8229(4)	5.8165(5)	5.8112(4)	5.8063(6)
c (Å)	4.9383(3)	4.9365(3)	4.9264(4)	4.9222(5)	4.9193(4)	4.9145(6)
β (°)	109.745(3)	109.739(4)	109.731(4)	109.719(7)	109.711(6)	109.705(8)
Cell Vol ($Å^3$)	298.75(3)	298.35(3)	296.40(3)	295.57(5)	294.97(4)	294.13(5)
Ca (*x*,0,*z*)	0.7253(6) 0.663(1)	0.7244(6) 0.664(1)	0.7246(6) 0.661(1)	0.7247(8) 0.663(2)	0.7239(7) 0.660(1)	0.7239(9) 0.655(2)
Mn1 (0,0,½)						
Mn2 (0,*y*,0)	0.249(1)	0.252(2)	0.249(2)	0.2459(8)	0.246(2)	0.244(2)
O1 (*x*,y,*z*)	0.1007(3) 0.2200(5) 0.3941(7)	0.0995(4) 0.2210(6) 0.3929(8)	0.1005(4) 0.2215(6) 0.3932(8)	0.0999(5) 0.2225(8) 0.392(1)	0.0996(4) 0.2211(7) 0.3941(9)	0.1033(6) 0.2198(9) 0.394(1)
O2 (*x*,½,*z*)	0.5957(4) 0.899(1)	0.5972(6) 0.899(1)	0.5957(6) 0.900(1)	0.5963(8) 0.902(2)	0.5964(7) 0.899(1)	0.5987(9) 0.900(2)
O3 (*x*,0,*z*)	0.6031(5) 0.9565(9)	0.6026(5) 0.959(1)	0.6050(5) 0.960(1)	0.6053(7) 0.956(1)	0.6056(6) 0.957(1)	0.6046(8) 0.955(2)

Table S3: *Rietveld refinement parameters for neutron diffraction data collected at 120 K between 2.6 GPa and 4.572 GPa using the PEARL diffractometer for $Ca_2Mn_3O_8$, refined using the C2/m model proposed by Ansell et al.[5] Note: U_{iso} were fixed to 0.01 Å^2. Values in parentheses indicate one standard deviation in the parameter.*

Parameter	**Pressure (GPa)**			
	2.600	**3.021**	**3.487**	**4.572**
χ^2	1.453	0.8481	0.8843	0.9740
wRp (%)	2.62	2.90	3.03	3.10
Rp (%)	2.97	3.34	3.51	3.64
a (Å)	10.940(1)	10.924(1)	10.912(1)	10.883(2)
b (Å)	5.8001(6)	5.7942(7)	5.7875(7)	5.7732(9)
c (Å)	4.9100(6)	4.9057(7)	4.9003(7)	4.8884(9)
β (°)	109.698(8)	109.663(9)	109.65(1)	109.67(1)
Cell Vol (Å^3)	293.33(5)	292.40(6)	291.44(7)	289.22(8)
Ca (*x*,0,*z*)	0.7252(9) 0.660(2)	0.725(1) 0.659(2)	0.725(1) 0.660(2)	0.724(1) 0.658(2)
Mn1 (0,0,½)				
Mn2 (0,*y*,0)	0.246(2) 0.1002(5)	0.241(3) 0.0984(6)	0.243(3) 0.0982(7)	0.253(3) 0.1003(8)
O1 (*x*,*y*,*z*)	0.1002(5) 0.2216(9) 0.394(1)	0.0984(6) 0.222(1) 0.394(1)	0.0982(7) 0.220(1) 0.394(2)	0.1003(8) 0.222(1) 0.396(2)
O2 (*x*,½,*z*)	0.5983(9) 0.900(2)	0.602(1) 0.901(2)	0.603(1) 0.903(2)	0.601(1) 0.903(2)
O3 (*x*,0,*z*)	0.6037(8) 0.955(1)	0.6043(9) 0.952(2)	0.607(1) 0.952(2)	0.603(1) 0.957(2)

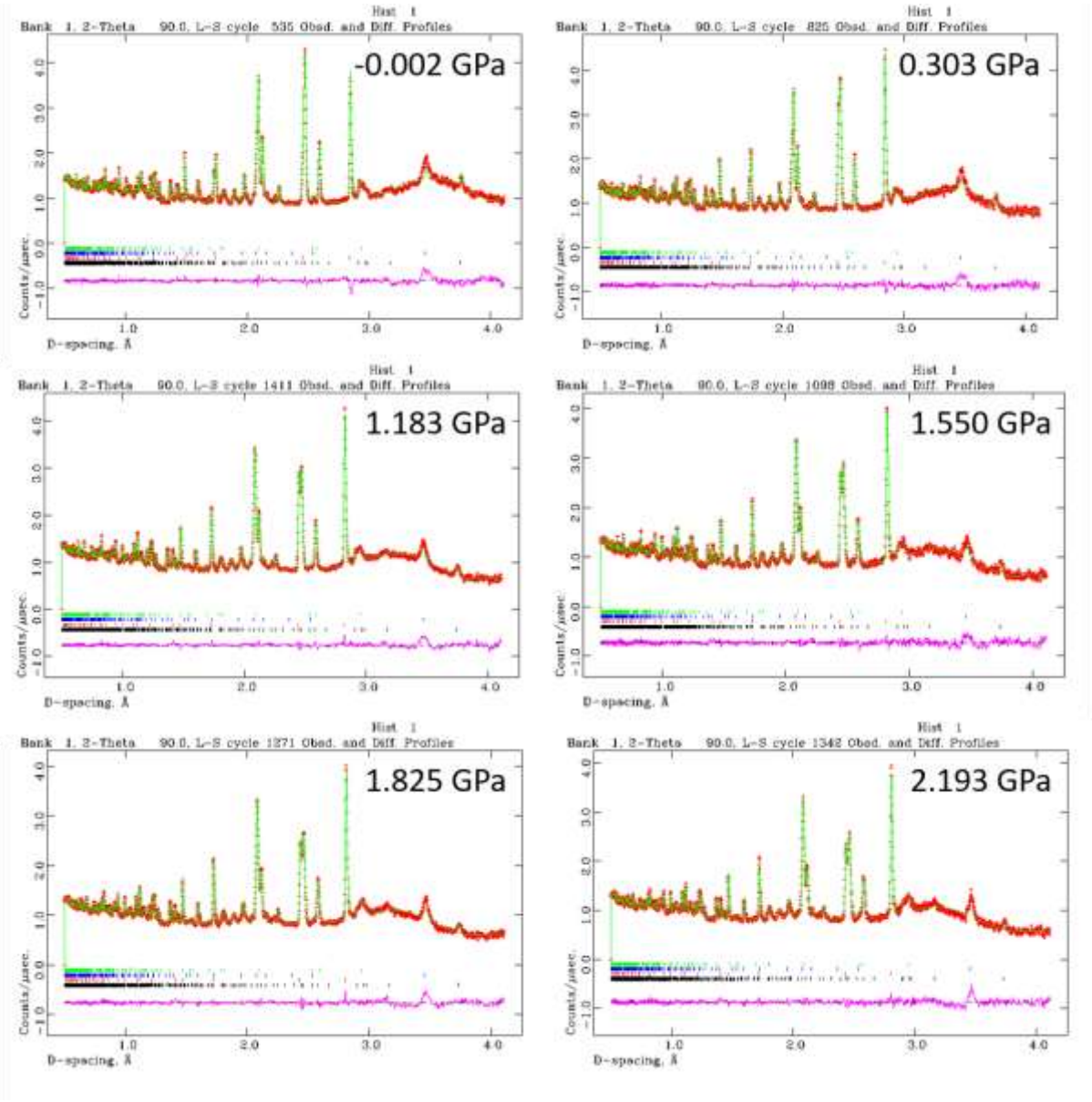

Figure S2: *Rietveld refinement of the powder neutron diffraction data collected for $Ca_2Mn_3O_8$ at 120 K at pressures between 0 GPa to 2.193 GPa refined using the space group C2/m and the model proposed by Ansell et al.*[5] *The red circles are the observed data, the green line is the calculated model and the pink line is the difference curve.*

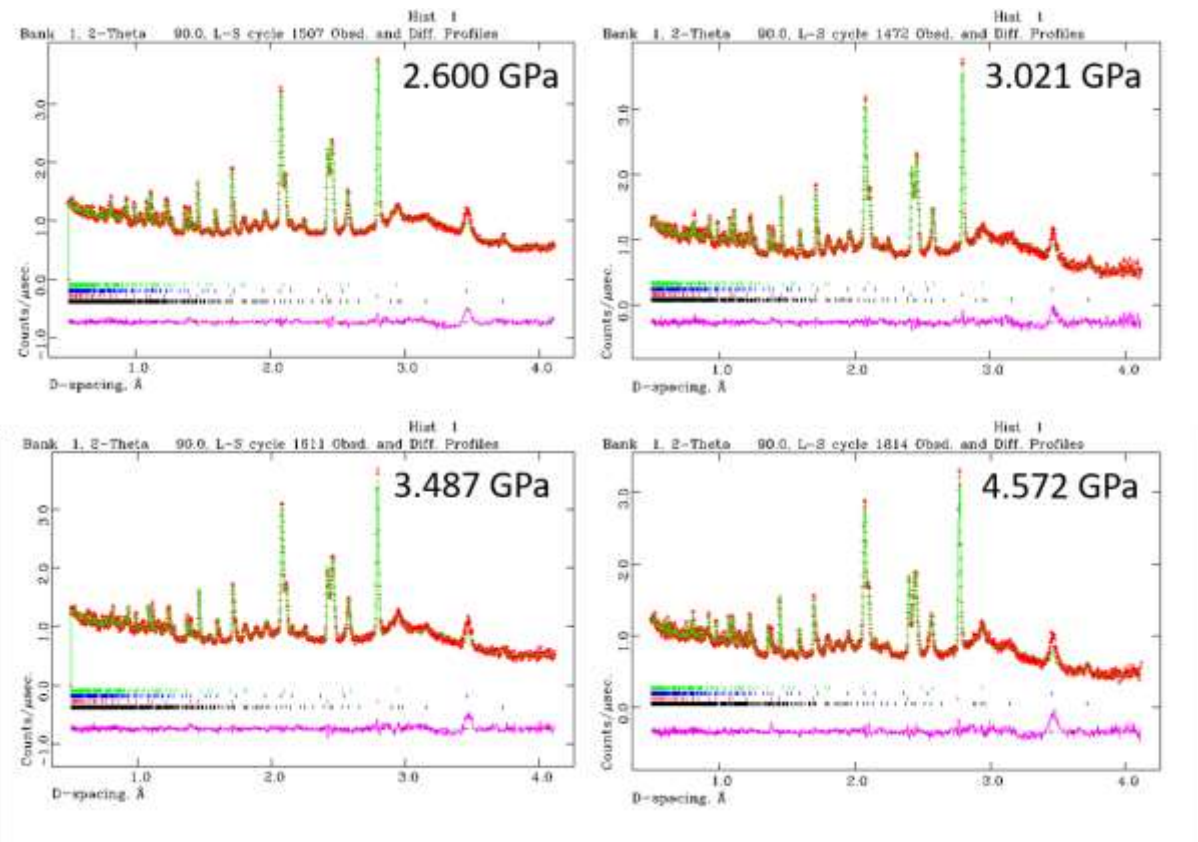

Figure S3: *Rietveld refinement of the powder neutron diffraction data collected for $Ca_2Mn_3O_8$ at 120 K at pressures between 2.600 GPa to 4.572 GPa refined using the space group C2/m and the model proposed by Ansell et al.*[5] *The red circles are the observed data, the green line is the calculated model and the pink line is the difference curve.*

Table S4: *Selected bond lengths and bond angles extracted from the Rietveld refinement parameters for neutron diffraction data collected at 290 K between 0 GPa and 6 GPa using the PEARL diffractometer for $Ca_2Mn_3O_8$. Values in parentheses indicate one standard deviation in the parameter.*

Bond lengths (Å)	**Pressure (GPa)**						
	0.092	**0.445**	**1.254**	**2.142**	**3.189**	**4.451**	**5.571**
Mn1-O1 (x4)	1.884(4)	1.876(4)	1.877(4)	1.878(4)	1.871(5)	1.858(5)	1.869(5)
Mn1-O2 (x2)	1.865(6)	1.878(6)	1.875(6)	1.867(5)	1.866(7)	1.889(6)	1.866(6)
Mn2-O1 (x2)	1.869(4)	1.869(4)	1.870(4)	1.866(4)	1.862(5)	1.878(4)	1.863(4)
Mn2-O2 (x2)	1.982(8)	1.997(7)	2.019(8)	1.987(7)	1.961(9)	1.992(8)	1.989(8)
Mn2-O3 (x2)	1.908(8)	1.896(8)	1.856(8)	1.874(8)	1.89(1)	1.862(9)	1.848(8)
Ca-O1 (x2)	2.454(8)	2.448(8)	2.462(8)	2.446(8)	2.452(9)	2.422(9)	2.410(9)
Ca-O1 (x2)	2.252(5)	2.253(5)	2.246(6)	2.240(5)	2.230(7)	2.239(6)	2.224(6)
Ca-O2	2.433(9)	2.413(9)	2.400(9)	2.401(9)	2.400(1)	2.34(1)	2.35(1)
Ca-O3	2.266(8)	2.281(8)	2.275(9)	2.274(8)	2.249(1)	2.250(9)	2.251(9)
Bond Angles (º)							
Mn1-O1-Mn2	100.0(3)	100.3(3)	101.0(3)	100.1(3)	99.7(3)	100.3(3)	100.7(3)
Mn1-O2-Mn2 (x2)	96.7(2)	95.8(2)	95.8(2)	96.2(2)	96.3(3)	95.2(3)	96.0(2)
Mn2-O2-Mn2	95.5(5)	95.1(5)	96.6(5)	96.0(4)	95.2(6)	96.5(5)	98.4(5)
Mn2-O3-Mn2	99.5(4)	99.5(4)	98.7(4)	99.8(4)	100.4(5)	98.4(5)	96.9(5)
Ca-O1-Ca	95.4(2)	95.0(2)	95.3(2)	95.6(2)	95.7(2)	95.9(2)	95.8(2)
Ca-O1-Mn1	103.2(2)	103.0(2)	102.8(2)	102.8(2)	102.8(2)	102.9(2)	102.5(2)
Ca-O1-Mn2	98.5(3)	98.6(3)	98.5(3)	98.2(3)	97.6(3)	97.4(3)	98.6(3)
Ca-O1-Mn1	128.0(2)	128.5(2)	128.2(2)	128.1(2)	128.0(3)	128.8(3)	128.2(3)
Ca-O2-Mn2	124.9(3)	124.3(3)	124.0(3)	124.9(3)	125.6(4)	124.1(4)	123.9(4)
Ca-O2-Mn1	161.0(4)	162.2(4)	161.7(4)	161.3(4)	160.8(5)	161.6(4)	160.5(4)
Ca-O2-Mn2 (x2)	96.1(2)	96.2(2)	96.4(2)	96.3(2)	96.6(2)	97.0(2)	97.0(2)
Ca-O3-Mn2 (x2)	124.6(2)	124.6(2)	124.8(2)	124.3(2)	124.2(2)	125.0(2)	124.9(2)

Table S5: *Selected bond lengths and bond angles extracted from the Rietveld refinement parameters for neutron diffraction data collected at 120 K between 0 GPa and 2.193 GPa using the PEARL diffractometer for $Ca_2Mn_3O_8$. Values in parentheses indicate one standard deviation in the parameter.*

Bond lengths (Å)	**Pressure (GPa)**					
	-0.002	**0.303**	**1.183**	**1.550**	**1.825**	**2.193**
Mn1-O1 (x4)	1.883(3)	1.879(4)	1.894(4)	1.884(5)	1.870(5)	1.868(6)
Mn1-O2 (x2)	1.895(5)	1.897(5)	1.896(5)	1.903(7)	1.889(6)	1.898(8)
Mn2-O1 (x2)	1.894(3)	1.886(4)	1.884(4)	1.876(5)	1.882(4)	1.882(6)
Mn2-O2 (x2)	1.955(7)	1.980(7)	1.946(7)	1.93(1)	1.939(8)	1.94(1)
Mn2-O3 (x2)	1.912(7)	1.888(8)	1.914(8)	1.93(1)	1.932(9)	1.93(1)
Ca-O1 (x2)	2.400(7)	2.422(8)	2.402(7)	2.41(1)	2.411(9)	2.39(1)
Ca-O1 (x2)	2.255(5)	2.256(5)	2.240(5)	2.240(7)	2.234(6)	2.226(7)
Ca-O2	2.383(8)	2.376(9)	2.382(9)	2.37(1)	2.39(1)	2.39(1)
Ca-O3	2.286(7)	2.286(8)	2.278(8)	2.25(1)	2.26(1)	2.28(1)
Bond Angles (º)						
Mn1-O1-Mn2	98.6(2)	99.5(3)	98.6(3)	98.4(4)	98.6(3)	98.3(4)
Mn1-O2-Mn2 (x2)	96.1(2)	95.7(2)	96.1(2)	95.8(3)	96.0(3)	95.2(3)
Mn2-O2-Mn2	95.9(4)	96.1(5)	96.1(5)	95.4(6)	94.6(5)	93.0(7)
Mn2-O3-Mn2	100.4(4)	100.0(4)	99.7(4)	99.8(6)	99.8(5)	100.5(6)
Ca-O1-Ca	96.1(2)	95.9(2)	96.0(2)	95.9(2)	95.6(2)	95.4(3)
Ca-O1-Mn1	105.6(2)	103.4(2)	103.2(2)	103.0(2)	103.3(2)	103.5(3)
Ca-O1-Mn2	98.0(2)	98.1(3)	98.2(3)	97.7(4)	97.7(3)	98.4(4)
Ca-O1-Mn1	129.0(2)	128.6(2)	128.9(2)	128.7(3)	129.3(3)	129.7(3)
Ca-O2-Mn2	124.7(3)	124.5(3)	125.0(3)	125.9(5)	125.1(4)	124.7(5)
Ca-O2-Mn1	160.5(3)	161.0(4)	160.2(4)	160.2(5)	160.9(4)	162.3(6)
Ca-O2-Mn2 (x2)	96.9(2)	97.0(2)	97.1(2)	97.5(3)	96.9(2)	96.89(3)
Ca-O3-Mn2 (x2)	124.8(2)	124.7(2)	124.4(2)	124.7(2)	124.6(2)	124.42(3)

Table S6: *Selected bond lengths and bond angles extracted from the Rietveld refinement parameters for neutron diffraction data collected at 120 K between 2.600 GPa and 4.572 GPa using the PEARL diffractometer for $Ca_2Mn_3O_8$. Values in parentheses indicate one standard deviation in the parameter.*

Bond lengths (Å)	**Pressure (GPa)**			
	2.600	**3.021**	**3.487**	**4.572**
Mn1-O1 (x4)	1.873(6)	1.858(7)	1.848(8)	1.862(8)
Mn1-O2 (x2)	1.896(7)	1.909(9)	1.92(1)	1.904(1)
Mn2-O1 (x2)	1.879(5)	1.870(6)	1.871(6)	1.883(7)
Mn2-O2 (x2)	1.95(1)	1.95(1)	1.96(1)	1.98(1)
Mn2-O3 (x2)	1.92(1)	1.95(1)	1.95(1)	1.87(2)
Ca-O1 (x2)	2.39(1)	2.40(1)	2.40(2)	2.39(2)
Ca-O1 (x2)	2.231(7)	2.237(8)	2.241(9)	2.21(1)
Ca-O2	2.36(1)	2.34(2)	2.33(2)	2.34(2)
Ca-O3	2.27(1)	2.26(2)	2.22(2)	2.27(2)
Bond Angles (°)				
Mn1-O1-Mn2	98.3(4)	98.4(4)	98.9(5)	98.9(5)
Mn1-O2-Mn2 (x2)	95.3(3)	94.0(4)	93.8(4)	94.2(4)
Mn2-O2-Mn2	94.3(6)	91.4(8)	92.2(9)	94.9(8)
Mn2-O3-Mn2	100.4(6)	101.0(7)	99.4(8)	99.8(8)
Ca-O1-Ca	95.6(2)	95.0(3)	95.0(3)	95.8(3)
Ca-O1-Mn1	103.0(2)	102.8(3)	103.3(3)	103.1(3)
Ca-O1-Mn2	97.9(4)	97.1(5)	97.4(5)	98.4(5)
Ca-O1-Mn1	129.4(3)	129.6(4)	129.5(4)	129.8(4)
Ca-O2-Mn2	125.3(5)	125.9(6)	125.1(7)	124.0(6)
Ca-O2-Mn1	162.0(5)	164.1(6)	163.7(7)	163/0(7)
Ca-O2-Mn2 (x2)	96.9(3)	97.0(3)	97.4(4)	97.3(4)
Ca-O3-Mn2 (x2)	124.7(2)	124.7(3)	125.2(3)	124.8(3)

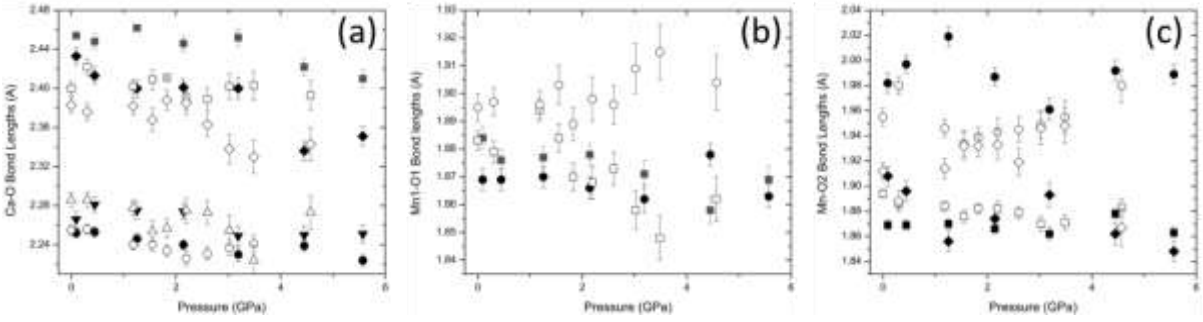

Figure S4: *Pressure dependence of (a) the Ca-O bond lengths where the squares and circles represent the Ca-O1 bond lengths, the diamonds the Ca-O2 bond lengths and the triangles the Ca-O3 bond lengths, (b) the Mn1-O1 (squares) and Mn1-O2 (circles) bond lengths and (c) Mn2-O1 (squares), Mn2-O2 (circles) and Mn2-O3 (diamonds) bond lengths extracted from the Rietveld refinement of neutron diffraction data collected for $Ca_2Mn_3O_8$ at 290 K (filled markers) and 120 K (open markers).*

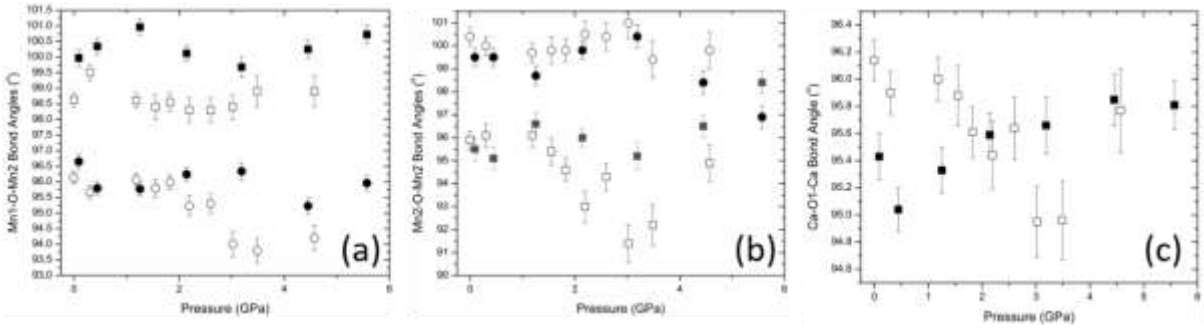

Figure S5: *Pressure dependence of (a) the Mn1-O1-Mn2 (squares) and Mn1-O2-Mn2 (circles) bond angles, (b) Mn2-O2-Mn2 (squares) and Mn2-O3-Mn2 (circles) bond angles and (c) Ca-O1-Ca (squares) bond angles extracted from the Rietveld refinement of neutron diffraction data collected for $Ca_2Mn_3O_8$ at 290 K (filled markers) and 120 K (open markers).*

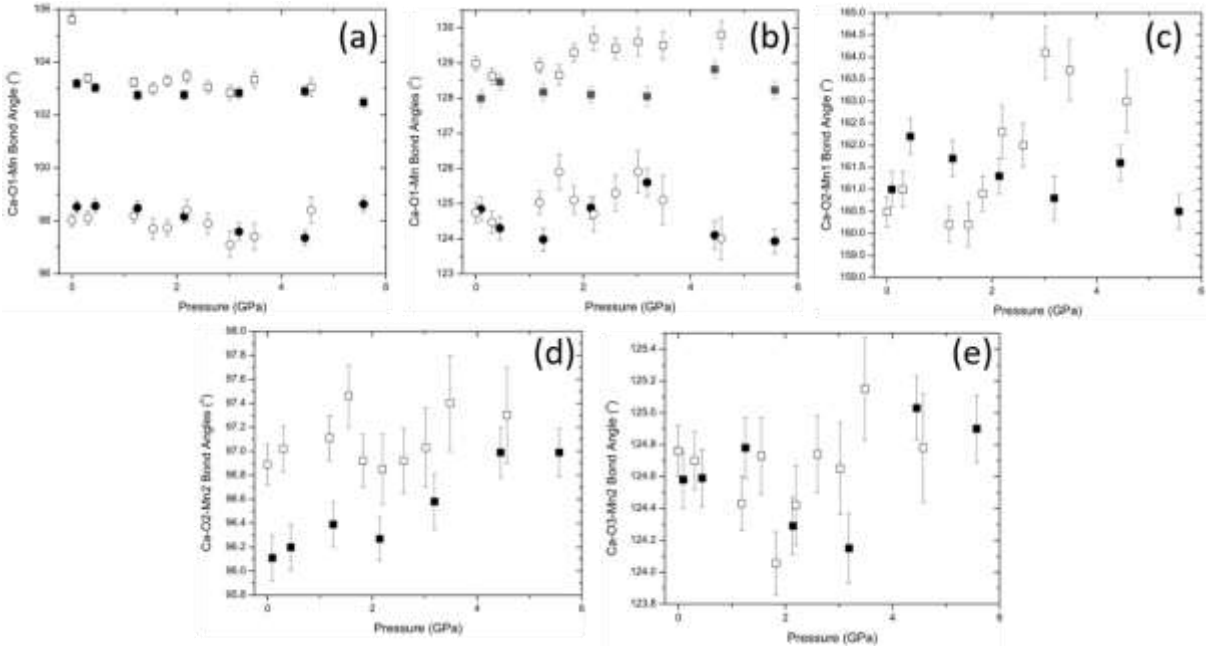

Figure S6: *Pressure dependence of (a) the short Ca-O1-Mn1 (squares) and Ca-O1-Mn2 (circles) bond angles, (b) the long Ca-O1-Mn1 (squares) and Ca-O1-Mn2 (circles) bond angles, (c) the Ca-O2-Mn1 (squares) bond angles, (d) the Ca-O2-Mn2 (squares) bond angles and (e) Ca-O3-Mn2 (squares) bond angles extracted from the Rietveld refinement of neutron diffraction data collected for $Ca_2Mn_3O_8$ at 290 K (filled markers) and 120 K (open markers).*

References

1. A. C. Larson and R. B. von Dreele, *Los Alamos National Report LAUR*, 1994, **96**, 86.
2. B. H. Toby, *J. Appl. Crystallogr.*, 2001, **34**, 210.

3. C. J. Howard, *J. Appl. Crystallogr.*, 1982, **15**, 615.
4. P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79.
5. G. B. Ansell, M. A. Modrick, J. M. Longo, K. R. Poeppelmeier, H. S. Horowitz, *Acta. Crystallogr. B.*, 1982, **28**, 1795